

CONVERSION OF FOSSIL FUELS TO LIQUID FUELS

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INTRODUCTION

Petroleum and natural gas production in the United States is under continuous study by organizations, both private and public, concerned with our energy supply. Over the years these studies have led to many predictions as to when synthetic liquid fuels would be needed. In the 1940's the United States became a net importer of petroleum, the excess of demand over supply coming from abroad. In 1941, for example, 1.402 billion barrels were produced and 1.486 billion barrels were consumed. Although there is no need to produce liquid fuels synthetically at the present time, it is comforting to have the know-how, just in case. Coal and oil shale are the logical raw materials since our mineable reserves are equivalent to trillions of barrels of oil, much of it near areas of consumption.

During the war years there was grave concern about our petroleum reserves, and a review of the facts at congressional hearings led to the Synthetic Fuels Act of 1944. From the research program supported by this legislation came significant developments in the processing of oil shale and the hydrogenation of coal and carbon monoxide. The laboratories at Rifle, Colo., and Laramie, Wyo., demonstrated improved mining methods and techniques for the conversion of oil shale to hydrocarbon products. At Bruceton, Pa., and Morgantown, W. Va., large research programs were carried out to demonstrate the methods of hydrogenation. At Louisiana, Mo., the demonstration plant contained a semi-commercial unit for the hydrogenation of coal and the latest concept, at that time, for the hydrogenation of carbon monoxide. The coal hydrogenation unit could produce 200 barrels product a day, and over 1.5 million gallons of gasoline were produced of which 1 million gallons were fleet tested by the armed services. Once the demonstration units at Rifle and Louisiana were in operation, economic studies were started, early estimates indicated costs of 9 cents a gallon for gasoline from oil shale and 14.5 cents a gallon for gasoline from coal.

In the period between 1949 and 1953, the economics of synthetic liquid fuels was evaluated by the Bureau of Mines, the National Petroleum Council, Ebasco Services, Inc., and the Bechtel Corporation. These studies, although starting with the same basic technological concepts, produced results which varied considerably. Some of the accountable differences are found in the financial structure assumed for the plants, the return on investment anticipated, and the cost of the mine, startup expenses, byproducts, and royalties. However, there was one definitive conclusion--none of the processes could produce a fuel that could compete with petroleum.

The National Petroleum Council² arrived at the following selling price for gasoline at the refinery:

Oil shale	14.7 cents a gallon
Gas synthesis	29.4 cents a gallon
Coal hydrogenation	36.3 cents a gallon

These costs assume 6 percent return on investment after taxes and limited credit for byproducts. Although gasoline from shale can be produced at a lower cost, the areas suitable for production are remote from major markets and transportation costs to the west coast would increase the delivered price.

Development of the processes for the formation of liquid fuels were continued under the Synthetic Liquid Fuels Act until 1955. Research was then continued as part of the Bureau's minerals research and development programs. The demonstration plants were discontinued in 1953.

Other processes that might be a source of liquid fuels were part of the research program. Particular attention was given to low temperature carbonization where the yields of oil and tar may be relatively high. However, like the synthesis processes, fuels made by carbonization are not economically competitive today.

The overall objectives were clear: For synthetic fuels to be competitive, major cost reductions were necessary; for conservation of resources, technology had to be improved; for national security, one or more processes should be on the verge of commercial development.

Coal Hydrogenation

Improvements in the direct hydrogenation of coal were geared to making the process less costly by looking for cheaper sources of hydrogen, improved catalysts, less severe operating conditions, and reaction schemes that would simplify the overall plant. Good catalysts were found that could be applied in very low concentrations, but impregnation of the dry coal was required. Emphasis had been placed on the use of dry coal to eliminate the costly steps in paste preparation and handling. Although conversion of the coal was high, the distillable oil product still required further processing to make it stable enough to be used as an automotive or aircraft fuel. Thus only negligible savings could be demonstrated. An attempt to eliminate some of the refining was made by hydrogenating coal in a high temperature, one-step process. The reaction rate could not be controlled at temperatures above 480° C unless the catalyst concentration was low, but then coking occurred.

Another approach was to provide longer reaction times at a much lower pressure and to use more catalyst. It was demonstrated that the conversion of hvcb coal at 2000 psig was about the same as that obtained at much higher pressures and that a distillable oil yield of the same magnitude could be recovered. Coal conversions, for example, were around 95 percent at 2000 psig, and the average yields of distillable oil were about 65 percent. A further consideration was the anticipated trend to gas turbines and heavier fuels that require less refining. It has been demonstrated that heavy fuel oils could be produced by hydrogenation as low as 1500 psig.^{3/} Economic gains could be realized from the reduced pressure operation requiring less gas compression and lighter construction. These advantages were partially offset by the increase in reactor volume required. Rough estimates indicated that the price of a gallon of distillate could be reduced from the NPC base figure of 36 cents per gallon to about 25 cents per gallon--a considerable saving but still far from competitive with gasoline from petroleum at 10 to 12 cents a gallon.

Gas Synthesis

The hydrogenation of carbon monoxide to liquid fuels is a gas phase catalytic process with several reaction systems possible. The first reaction systems were fixed beds with low throughput, but it was not long before improved reactors were

developed. Among the later systems were the fluidized bed, oil circulation, slurry, and hot gas recycle. Fluidized bed reactors were not investigated by the Bureau of Mines for the synthesis reaction because private industry was developing them. The Bureau concentrated on the latter three processes to evaluate effectiveness, life, and selectivity of catalysts and economics of the systems. For one reason or another all were eliminated except the hot gas recycle process which has prevailed because of catalyst shape developments which reduced pressure drop to a negligible value and operating flexibility. Even at high recycle rates of 10 to 30 volumes of recycle gas per volume of fresh feed gas, the recompression costs remain relatively low. The improvements that made the difference were activated steel lathe turnings having about 95 percent of void space in a reactor, parallel plate assemblies with the catalyst flame sprayed on the surface, and the latest operable system which merely has the catalyst flame sprayed on the wall of the reactor. Heat transfer problems in the last configuration are limited to the rate at which the heat of reaction can be transferred through the pipe wall. Reactors of this advanced type are more versatile than previously mentioned designs because they may be used for liquid or gas production. The other systems capable of this bi-functionality are the fluidized bed and fixed bed reactors. The product composition can be altered by changing the catalyst composition or sometimes its pretreatment to make liquid or gaseous hydrocarbons or oxygenated compounds. Regardless of the reaction system, it still takes about 650 cubic feet of synthesis gas to make a gallon of liquid product and 4000 cubic feet of carbon monoxide and hydrogen to make 1000 cubic feet of methane. Using a synthesis gas cost of 15 cents per thousand cubic feet from coal at \$4 a ton, the contribution of gas to the total cost is already 9.8 cents per gallon, or 60 cents per 1000 feet of high Btu gas.

Oil Shale

Shales that will yield oil on pyrolysis are widely distributed in the United States, but the deposit of most immediate interest as a possible source of liquid fuels is in Colorado. This deposit in the Green River Formation is the world's largest reserve of hydrocarbon material. The deposit in Colorado is the smallest in area, about 1,500 square miles, but represents the largest reserve, about 600 billion barrels of oil in beds that will yield an average of 25 gallons per ton.^{4/} The Utah and Wyoming deposits have not been completely evaluated but represent roughly 120 billion and 40 billion barrels of oil, respectively. The oil produced differs from petroleum in some important respects, but it can be refined by suitable processes to yield liquid fuels and other products now obtained from petroleum.

Mining costs, computed during the period of operation in the 1940's, ranged between 47 and 56 cents per ton.^{2/} They included underground labor, supplies, depreciation, taxes, and administrative overhead. It is difficult to translate these costs to the present because improvements in mining techniques and equipment, such as rotary drills and ammonium nitrate based explosives, tend to offset increased labor costs and capital investment. The mining method as developed is applicable to cliff-face locations in the Colorado River drainage area. Most of the huge reserve in the Piceance Creek basin of Colorado is in thicker beds away from the cliff face and will require the development of special techniques for recovery.

The Bureau and several cooperating organizations have conducted crushing tests on oil shale, using jaw, gyratory, impact, and roll-type equipment. Resulting data have proved useful for some design purposes but are probably inadequate for exact design of a commercial oil-shale crushing plant. The tough, elastic Green River oil shale tends to form slabs that present screening and handling problems.

More than 2,000 oil-shale retorting systems have been patented throughout the world, but these may be grouped into a few classes on the basis of method of heat transfer (Table 1).

TABLE 1.- Classification of retorts

- I. Heat is transferred to the shale through a wall.
- II. Heat is transferred to the shale from combustion of product gases and residual carbon within the retort.
- III. Heat is transferred to the shale by passing previously heated gases or liquids through the shale.
- IV. Heat is transferred to the shale by mixing it with hot solids.

No single process is best for use under all conditions. Research is being conducted by both Government and industry in an effort to develop the technology needed to produce fuels economically from Green River oil shale. Three processes have received most recent attention. Two of these, the gas-combustion process developed by the Bureau of Mines and the process of Union Oil Company of California, use combustion gases for heat, whereas the third one, a process developed by the Oil Shale Corporation (Tosco), retorts the shale by contact with heated ceramic or metal balls.

In the gas-combustion process an upward-flowing stream of gas contacts a descending bed of broken shale. Recycled product gas entering the bottom of the retort absorbs heat from the retorted shale. At an intermediate point, air is introduced to burn the gas and some residual carbon on spent shale. The hot gases heat the shale to produce oil that leaves the retort with the gases as a fine mist. Attractive features of this process are high thermal efficiency, oil yield, and retorting rate. Development of this process was discontinued in 1956 before it had been completely perfected but has recently been resumed as the result of leasing the Anvil Points Facilities of the Department of Interior to the Colorado School of Mines Research Foundation. Through a subsequent contract with the Foundation, Socony Mobil Oil Company and Humble Oil and Refining Company are conducting research to complete development of the process.

The Union Oil Company retort is a countercurrent, moving bed type in which a rock pump at the base of the retort forces the shale upward through the retort. Heat for retorting is produced by the combustion of the carbon on the spent shale using air drawn down through the retort. Oil vapors in the gas stream leaving the retorting zone are condensed on the cold shale in the lower part of the retort. This process has essentially the same advantages as the gas-combustion process.

The Tosco process utilizes a horizontal rotating kiln in which pulverized raw shale is heated by contact with preheated, closely sized metal or ceramic balls. Carbon residue on the spent shale is used as fuel for reheating the balls. This retort will presumably form the basis for commercial operations that have been announced by Colony Development Corporation, which is a joint venture of Standard Oil Company of Ohio, Cleveland Cliffs Iron Company, and the Oil Shale Corporation.

As an alternative to the preceding processes, retorting oil shale in place in the formation is a possibility. Because this approach involves a different set of costs from those for mining, crushing, and surface retorting, it may be a more economical way to produce shale oil. Further, it should be applicable to many deposits not readily amenable to the mining approach and would eliminate the necessity for disposing of spent shale. However, development of the process presents formidable research problems. For example, oil shale is essentially impermeable, so one of the first problems is to create and maintain suitable permeability. Fracturing by conventional petroleum techniques and by nuclear explosives is being investigated. One drawback is that oil shale expands when heated and may result in the closing of the required combustion path.

Oil produced from shale of the Green River Formation frequently has properties that require the application of degradation processes, such as visbreaking, before the oil can be transported conveniently by pipeline. Also, these properties present

some problems in the application of standard petroleum refining processes. For example, the nitrogen content of 2 percent, which is particularly high by petroleum standards, reduces the efficiency of catalytic processing techniques, and its presence in products promotes instability. Hence, special refining techniques are required. Hydrogenation is an effective process^{6/} for removing nitrogen, sulfur, and oxygen from shale oil and for producing excellent yields of high quality jet, diesel, and distillate fuels. Such hydrogenated oils also are satisfactory charging stocks for catalytic cracking and reforming processes^{7/} and may be suitable for use in manufacturing lubricants. Because of the potentialities of hydrogenation, most of the Bureau's recent refining research has been devoted to this method.

Because shale oil differs in composition from most petroleum, converting it to some products may result in byproducts not commonly obtained from petroleum, at least not in as large quantities. Among these may be phenols, pyridines, and ammonia. Others that are also commonly obtained from petroleum are hydrogen sulfide, sulfur, and specific olefinic or aromatic hydrocarbons. In addition to the byproducts from shale-oil processing, others may result from the retorting process. Because the exact byproducts obtained in any commercial operation will depend on details of the process used, their impact on the process is difficult to predict.

Bituminous Sands and Other Hydrocarbons

Deposits of outcropping bitumen-impregnated rocks and near-surface deposits of heavy crude oils in the United States are attracting attention as sources of fuels. Interest in bituminous sand deposits of the United States stems from extensive studies of the world's largest deposit--the Athabasca tar sands in Canada--that culminated in a commercial 45,000-barrel-per-day plant now being constructed by Great Canadian Oil Sands, Ltd., in northeastern Alberta Province.

The scattered occurrences of bitumen-impregnated rocks in the United States, including Alaska, have not been evaluated in detail; potential reserves in place are roughly estimated to be about 10 billion barrels,^{8/} of which the largest deposits in Utah, Texas, and California represent about 2 to 3 billion barrels of bitumen in place. A survey of information available on these domestic occurrences has been made by Ball Associates, Ltd., under a contract with the Bureau of Mines. Results of the survey will be published.

The only commercial production of fuels from a nonconventional source utilizes gilsonite, a hydrocarbon occurring in limited quantity in the Uinta basin in Utah.^{9/} For several years, the American Gilsonite Company mined about 1,000 tons of gilsonite daily and transported the crushed solid material in a water slurry 72 miles by pipeline to its refinery. Efficient hydraulic methods developed for mining and transporting the gilsonite, including boring machines for drilling large-diameter (up to 62 inches) tunnels and shafts, offer advantages for recovering other minerals such as coal. At the refinery, the crushed gilsonite is melted, mixed with hot recycle oil, and refined into 1,700 barrels of gasoline and 300 tons of metallurgical grade coke per day.

For several years natural gas was considered as the raw material for the production of synthetic liquid fuels and waxes using the Fischer-Tropsch synthesis. In the 1940's natural gas had not yet become the preferred fuel for home heating and industrial firing, partly because an adequate pipeline system was not in existence. Large quantities of natural gas near the source of supply could be contracted for at about five cents per thousand cubic foot. Consumption was around 2 trillion cubic feet per year. Most of the major oil companies and engineering companies developed workable processes for converting natural gas to higher hydrocarbons and had worked out most of the analyses of their products. The only domestic synthetic liquid fuel plant to get off the ground was the one built at Brownsville, Tex., by Carthage Hydrocol in 1950. The Amoco Chemicals Corp. took over the plant in 1953

and after engineering modifications declared the process as being technically sound. However, by 1957 the consumption of natural gas had risen to 10 trillion cubic feet. Raw material and other costs made the process uneconomical, and the plant at Brownsville, Tex., was shut down in 1957.

Today the only large synthetic fuels plant known to be in operation is the SASOL plant near Johannesburg, South Africa. After several years the operation is reported to be in the black and expansion is continuing. Economic operation is possible only because the coal is inexpensive and transportation costs are high to bring petroleum products from the coast. Coal is delivered at the plant for less than \$1 a ton. Gasoline sells for 25 cents per gallon at the refinery yielding a net profit of about 8 cents a gallon. About 40 percent of the revenue from the SASOL units come from the sale of byproducts used for the manufacture of synthetic rubber, plastics, waxes, and fertilizers.

The Office of Coal Research, established in 1961, includes liquid fuels as one of its objectives. An early contract was with the FMC Corp. to convert coal by multistage carbonization into a liquid material to carry the char and other particles in a pipeline. By 1964 small scale laboratory tests had been completed, and a 100 lb per hour plant was scheduled for operation.^{10/} One of the experimental objectives has been to convert as much as possible of the 41 percent of volatile matter in Elkhol coal to liquid products. The highest tar yields reported have been less than half the estimated total.

The General Electric Co. had planned to use a high-voltage corona discharge as an agent in the hydrogenation of coal into a liquid, gas, or chemicals. Small scale experiments indicated that insufficient activation was produced by the corona discharge, and work on a larger scale has been suspended. An economic estimate presented last year^{11/} indicated that the break even point was at a product selling price of 2 cents per pound and a corona efficiency of 1.5 kwh/lb coal reacted.

Project gasoline was first evaluated by the Ralph M. Parsons Co. and was considered to be feasible. The process as proposed by the Consolidation Coal Co. consists principally of extraction of a large part of coal in a recycle solvent, filtration, separation of the extract from the recycle oil, and upgrading of the extract by catalytic hydrogenation. Estimates based on studies up to the present time indicate that a commercial plant could make gasoline at a cost of 13.6 cents a gallon.^{12/} Hydrogen is a costly item in the process, and another OCR contract with the MHD Research Corp. anticipates the production of hydrogen in a plasma for 25 cents per thousand cubic feet compared with 40 cents or more per thousand cubic feet by conventional methods.

The Atlantic Refining Co. has proposed a process to mix coal and residual fuel and to treat the mixture as a refinery feed stock. The coke residue would be burned in an electric-generating station. It is estimated that the combined feed to the coking unit would recover about 30 percent of the coal as liquid product, thereby reducing the amount of crude charged to the refinery by about 30 percent.

Conclusions

Supplies of crude petroleum and natural gas, although abundant, are not inexhaustible, and provision is being made for the time when our vast coal and oil shale reserves will be called upon to supply a significant quantity of liquid fuels. The Bureau's approach on coal research has been to continue theoretical and practical studies to reduce costs by improving stages in the process or by developing new processes. A flexible, integrated plant might emphasize production of different fuels or byproducts under different economic conditions and even at different times of the year. To reduce hydrogen requirements, an alternative is the partial conversion of coal whereby most of the hydrogen is utilized as a hydrocarbon product. The char product is used for generating power or making additional hydrogen by gasification.

In recent years, oil shale research by the Bureau of Mines has been limited to small scale laboratory studies on refining and analysis. Large scale research and commercial development have been resumed within the last year. The cost of producing gasoline from oil shale is almost competitive with gasoline from petroleum on the west coast. One of the main problems is the isolated location of major deposits.

The recent process developments discussed have added more to refined technology rather than provide significant savings in cost. As research is continued, more savings will probably be shown but not large ones unless they occur in the areas of gasification or reaction kinetics. It has been amply demonstrated both in the United States and elsewhere in the world, that liquid fuels can be made from coal. Except in isolated cases, costs are too high for coal to be a real contender with petroleum at current prices.

Only by continued research will the remaining problems be solved. Research on both the fundamental level and engineering level will be continued in the hope that a major breakthrough on the costly steps can be achieved.

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